Stefan Krakowiak, Pawe³ Œlepski, Andrzej Krakowiak

APPLICATION OF HARMONIC TECHNIQUES TO EVALUATION OF PITTING CORROSION

Technical University of Gdansk, Faculty of Chemistry, Department of Anticorrosion Technology
PL-80-952 Gdañsk-Wrzeszcz, ul. G. Narutowicza 11/12

Summary: In this paper an attempt of application of ac methods to evaluation of alloy steels susceptibility to pitting corrosion has been presented. A sine signal of frequency equal to 1 Hz was overlapped on DC signal. Due to simultaneous, digital registration of perturbation and response signals of an investigated system a continuous change of impedance and capacitance moduli was obtained during classical, cyclic polarisation. There is a possibility of determination of a polarisation curve as well as all characteristic potentials (E_{np}, E_{cp}) on the basis of one experiment. Analysis of registers allows to obtain continuous changes of impedance and capacitance moduli during polarisation of alloy steels.

Key words: *Pitting corrosion, impedance, capacitance, stainless steels*

INTRODUCTION

DC methods gained wide popularity in pitting corrosion investigations. Evaluation of alloy steels and nickel alloys susceptibility to pitting corrosion using cyclic polarization is currently a standardized method [1]. It allows to find characteristic potentials of pitting corrosion. The susceptibility of alloy steels to pitting corrosion is a function of the quality of the passive layer formed on the surface. The electrical properties of the passive layer allow application of electrochemical impedance spectroscopy in investigation of the passive layers.

Despite serious limitations, electrochemical impedance spectroscopy is employed to investigate different stages of pitting corrosion. Oltra and Keddam compared the results of impedance measurements with a theoretical model of pitting corrosion [2, 3].

Interpretation of capacitance changes of the passive layer on alloy steels is the second independent approach to results of impedance investigations. Marsh et al. presented results of investigations by electrochemical impedance spectroscopy of duplex type alloy steels, being widely introduced in maritime conditions. The investigations have been carried out by polarizing samples of examined steels in a wide range of potential [4]. Devaux et al. presented the concept of complex capacitance based evaluation of the results acquired by electrochemical impedance spectroscopy. On the basis of the spectra presented in real capacitance-imaginary capacitance system one can describe the structure of the passive layer and capacitance of its particular components. This paper presents results of the investigations performed on alloy steels perturbed with a signal composed of linearly changing potential and one 1 Hz sinusoid.

EXPERIMENTAL

Measurements were performed in 0.1 M NaCl solution. The solution was prepared from threefold-distilled water and pure sodium chloride. 304L and 316L steels were examined; their chemical composition is given in tab. 1.

Tabl.1. Chemical compositions of investigated stainless steels

Stainless steel	Cr	Ni	Mo	others
304L	**19.7**	**9.0**	**-**	**C – 0,03**
316L	**17.1**	**10.7**	**2.20**	**C – 0.02**

The investigation was carried out using a set-up assembled in The Department of Anticorrosion Technology. AC signal was generated by analog-digital card AT-MIO - 16E - 1 and to register current and potential signals analog-digital cards PCI 6052 E, produced by The National Instruments, were employed. As a current-voltage converter EP - 20 potentiostat, produced by ELPAN, was used. Schematic representation of the measurement set-up is given on fig.1.

Values of investigated characteristic potentials were determined with cyclic polarisation method ...

Steel electrodes, each of an area 0.5 cm^2, were prepared by polishing with abrasive papers of gradation from 180 to 800. In the next stage the samples were rinsed with distilled water and degreased in acetone. The electrodes were exposed to laboratory conditions for an hour before examination.

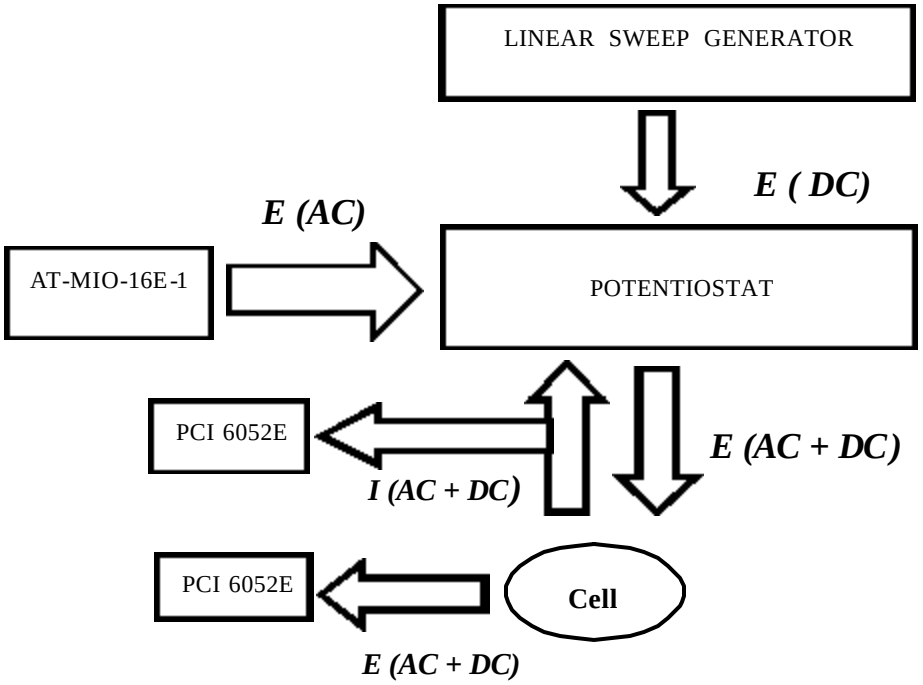

Fig.1. Scheme of an experimental set-up used in the investigations

RESULTS

Fig. 2 presents an exemplary part of perturbation signal, being a composition of linearly changing potential and sine signal (E), and corresponding response signal (I). Registration of the signals allows, at further stages of the analysis, to acquire interesting for us information concerning changes of impedance, capacitance and also characteristic potentials of pitting corrosion - after filtering out the variable component.

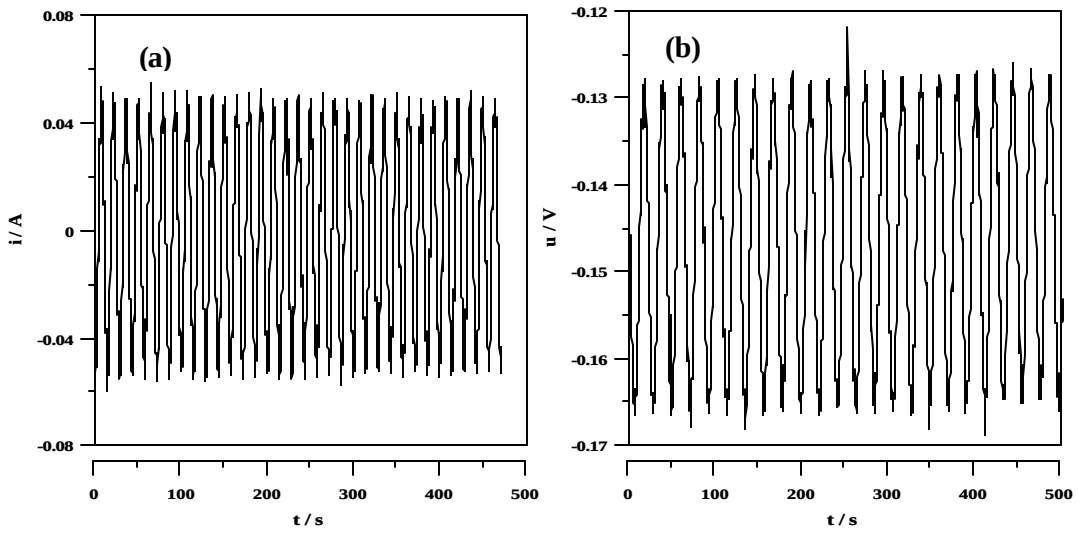

Fig. 2. Exemplary fragments of perturbation (a) and response (b) signals obtained for 304L stainless steel

On Fig.3 there are presented impedance modulus changes for investigated alloy steels under anodic polarisation, determined on the basis of registered perturbation and response signals. Due to digital registration it is possible to record continuous changes of the parameters being in the scope of the interest during the investigation.

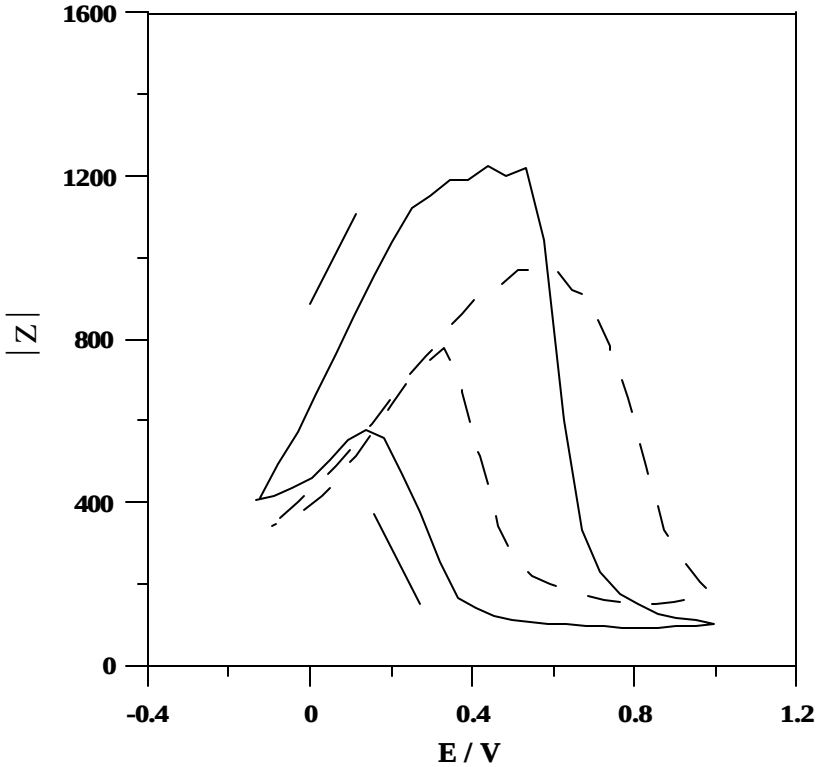

Fig.3. Dependence of impedance modulus from potential for 304L (—) and 316L (- - - -) stainless steels

During anodic polarisation, when steel is in the passive state, an increase in impedance modulus connected with a growth of the passive layer can be observed. In a metastable state one can distinguish fluctuations of impedance modulus followed by its fast drop related to a development of pits on electrode's surface. Characteristics for 304L and 316L steels are similar as both steels are susceptible to pitting corrosion in the conditions of investigation.

Having continuous changes of impedance modulus as well as of particular components and employing simple calculations it is possible to observe variation of capacitance of investigated steels.

Fig.4 depicts changes of passive layer capacitance of investigated steels during potential shift towards anodic direction. Initially a decrease in capacitance is observed which can be connected with cathodic polarisation of the sample. Applied measurement procedure assumes polarisation of the sample towards cathodic direction starting from 0.1V below the corrosion potential till the moment when 1 mA current is registered in the system. An increase in capacitance in anodic direction is connected with the growth of the passive layer or with its possible external decomposition.

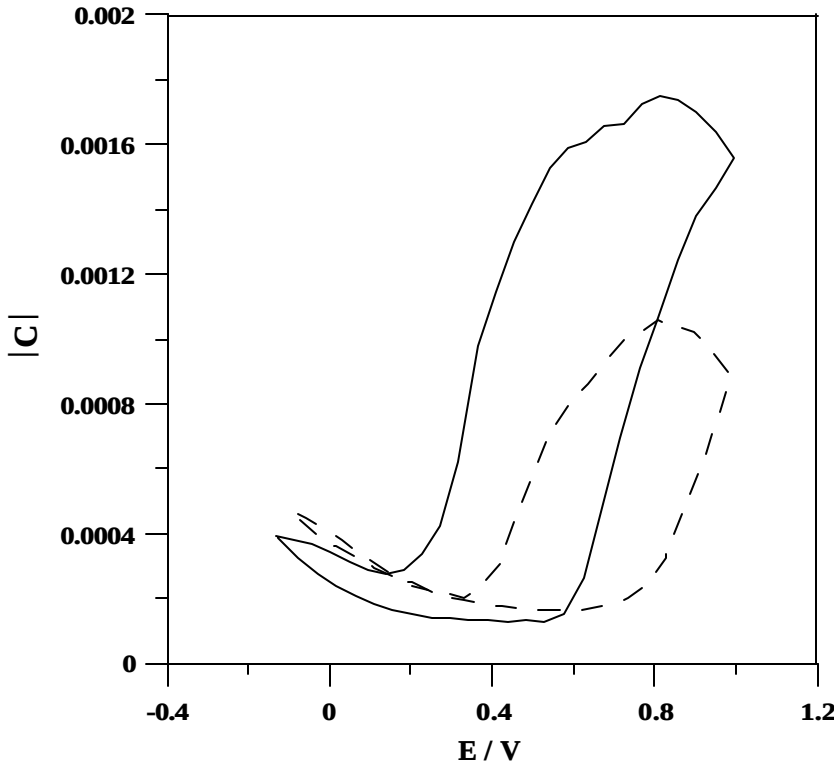

Fig.3. Dependence of capacitance modulus from potential for 304L (—) and 316L (- - - -) stainless steels

Figs. 5, 6 show cyclic anodic polarisation curves acquired after filtering out the variable component from obtained register. Typical characteristics for auto passive systems were recorded. Near break-through potential (E_b) there are registered current fluctuations, which are connected with appearance and passivation of unstable pits. The shape of return curve points at the susceptibility of both steels to pitting corrosion in the environment of investigation.

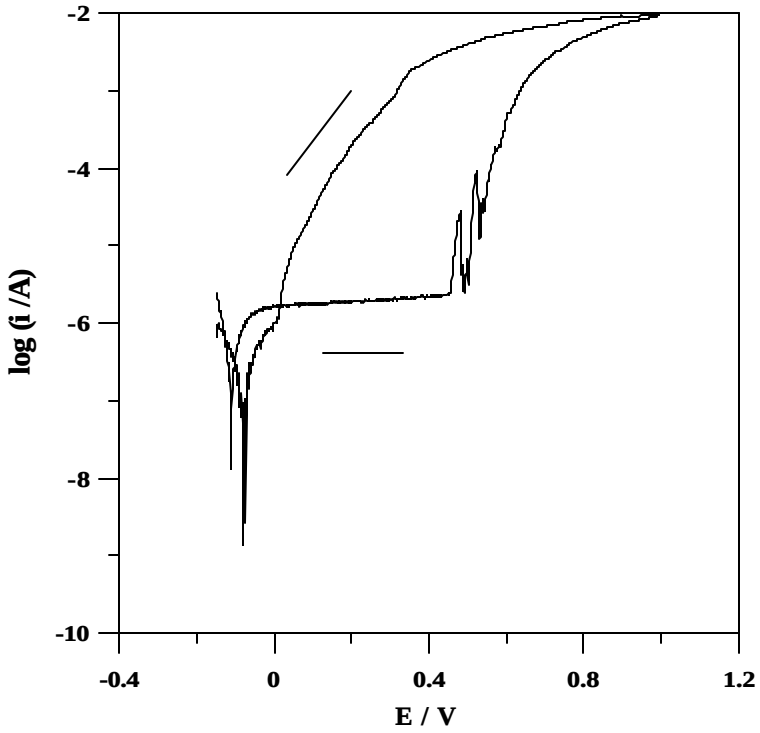

Fig. 5. Cyclic polarisation curve obtained for 304L steel by extraction of DC signal from the register

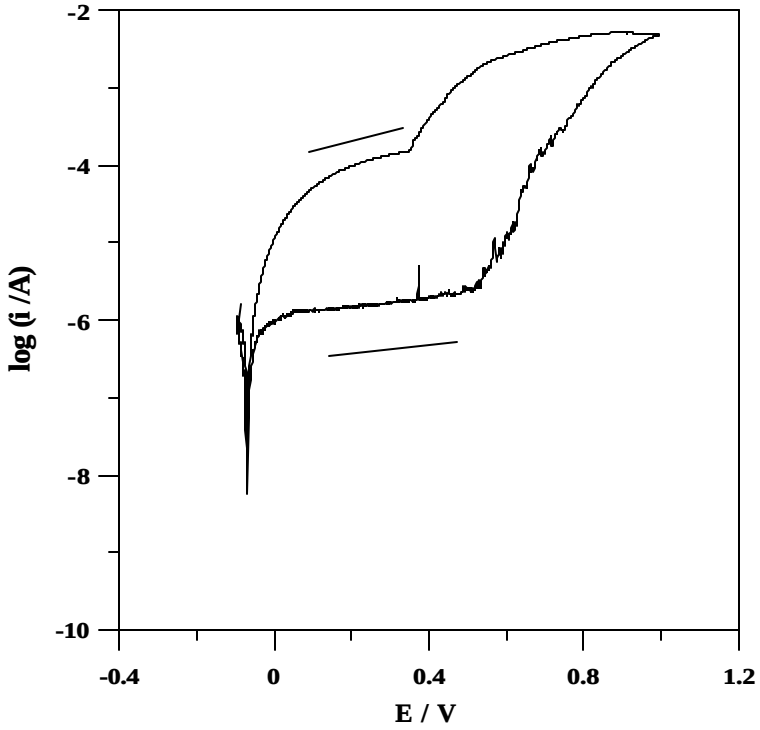

Fig. 6. Cyclic polarisation curve obtained for 316L steel by extraction of DC signal from the register

Values of pitting corrosion resistance determined on the basis of statistical analysis [6] of the polarisation curves obtained by both methods are similar. The values are presented in tab. 2.

Tab.2. Values of characteristic potentials obtained by independent methods

	$CP_{classic}$		CP_{new}	
Stal	E_b	E_{cp}	E_b	E_{cp}
Stal 304L	0.480	0.01	0.512	-0.01
Stal 316L	0.560	-0.03	0.650	-0.02

CONCLUSIONS

Application of digital methods of signal generation and registration allows to obtain continuous impedance and capacitance changes for steels being in the passive state as well as subjected to pitting corrosion. Perturbation with a signal that is a composition of linearly changing potential and sine signal increases the scope of information acquired in one experiment. Conducted researches are the introduction to application of the presented set-up to perturbation of examined system with a packet of sine signals. It will allow to investigate a non-stationary process of pitting corrosion.

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